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PREFACE

Transition metals (TMs) are 'elements whose atoms have partially filled d-shell, or which can give rise to cations with an incomplete d-shell'. In TMs, the d-shell overlaps with next higher s-shell. Most of the TMs exhibit more than one (multiple) oxidation states. Some TMs, such as silver and gold, occur naturally in their metallic state but, most of the TM minerals are generally oxides. Most of the minerals on the planet earth are metal oxides, because of large free energies of formation for the oxides. The thermodynamic stability of the oxides is determined from the *Ellingham diagram*. Ellingham diagram shows the temperature dependence of the stability (free energy) for binaries such as metal oxides. Ellingham diagram also shows the ease of reducibility of metal oxides.

TM oxides of general formulas MO, M_2O_3, MO_2, M_2O_5, MO_3 are known to exist, many of them being the ultimate products of oxidation in air in their highest oxidation states. In addition, TM oxides also exist in lower oxidation states which are prepared under controlled conditions. The nature of bonding in these oxides varies from mainly ionic (e.g. NiO, CoO) to mainly covalent (e.g. OsO_4). Simple binary oxides of the compositions, MO, generally possess the rock salt structure (e.g. NiO), while the dioxides, MO_2, possess the rutile structure (e.g. TiO_2); many sesquioxides, M_2O_3, possess the corundum structure (e.g. Cr_2O_3). TMs form important ternary oxides like perovskites (e.g. $CaTiO_3$), spinels (e.g. $MgFe_2O_4$) and so on. In TM oxides, the valence (outer) d-shell could be empty, d^0 (e. g. TiO_2), partially filled, d^n ($1 \leq n \leq 9$) (e.g. TiO, VO, NiO etc.) or completely filled, d^{10} (e.g. ZnO, CdO, Cu_2O etc.). The outer d electrons in TM oxides could be *localized* or *delocalized*. Localized outer d electrons give insulators/semiconductors, while delocalized/itinerant d electrons make the TM oxide 'metallic' (e.g. ReO_3, RuO_2). Partially filled d^n states are normally expected to give rise to itinerant (metallic) electron behaviour. But most of TM oxides with partially filled d shell are insulators because of special electronic energy (correlation energy) involved in d electron transfer to adjacent sites. Such insulating TM

oxides are known as *Mott insulators* (e. g. NiO, CoO etc.). Certain TM oxides are known to exhibit both localized (insulating) and itinerant (metallic) behaviour as a function of temperature or pressure. For example, VO_2 shows a insulator–metal transition at ~340K. Similar transitions are also known for V_2O_3, metal-rich EuO and so on.

The chemical composition and bonding of TM oxides, which determine the crystal and electronic structures, give rise to functional properties. Table 1 gives representative examples. Properties like ionic conductivity and diffusion are governed by both the crystal structure and the defect structure (point defects)**,** whereas properties such as magnetism and electron transport mainly arise from the electronic structures of the materials. Accordingly, TM oxides provide a platform for exploring functional material**s** properties. Among the various functional material**s** properties exhibited by transition metal oxides, the present thesis is devoted to investigations of lithium ion battery cathodes, inorganic pigments and magnetic perovskites.

Over the years, most of the lithium containing first row transition metal oxides of rock salt derived structure have been investigated for possible application as cathode materials in lithium ion batteries (LIBs). First major breakthrough in LIBs research was achieved by electrochemically deinserting and inserting lithium in $LiCoO_2$. A new series of cathode materials for LIBs were prepared by incorporating excess lithium into the transition metal containing layered lithium oxides through solid solution formation between Li_2MnO_3–$LiMO_2$ (M = Cr, Mn, Fe, Co, Ni), known as lithium-rich layered oxides (LLOs). LLOs exhibit improved electrochemical performance as compared to the corresponding end members and hence received significant attention as a potential next generation cathode materials for LIBs in recent times. $LiCoO_2$ (*R-3m*) crystallizes in the layered α-$NaFeO_2$ structure with the oxygens in a ccp arrangement. Li^+ and Co^{3+} ions almost perfectly order in the octahedral sites (3a and 3b) to give alternating (111) planes of LiO_6 and CoO_6 octahedra.

Table 1. Materials properties exhibited by representative TM oxides.

Property	Example(s)
Ferroelectricity	$BaTiO_3$, $PbTiO_3$, $Bi_4Ti_3O_{12}$
Nonlinear Optical Response	$LiNbO_3$
Multiferroic response	$BiFeO_3$, $TbMnO_3$
Microwave dielectric properties	$Ba_3ZnTa_2O_9$
Relaxor Dielectric Properties	$Pb_3MgNb_2O_9$,
Colossal Magnetoresistance	$Tl_2Mn_2O_7$
Metallic 'Ferroelectricity'	$Cd_2Re_2O_7$
Superconductivity	AOs_2O_6(A = K, Rb, Cs)
Redox deinsertion/insertion of lithium	$LiCoO_2$
Photocatalysis/water splitting	TiO_2
Pigment	$Ca_{(1-x)}La_xTaO_{(2-x)}N_{1+x}$ (yellow-red), $YIn_{1-x}Mn_xO_3$ (blue)
Metallic Ferromagnetism	CrO_2
Antiferromagnetism	NiO, $LaFeO_3$
Zero thermal expansion	ZrW_2O_8

The reversible capacity of $LiCoO_2$ in common LIBs is relatively low at around 140 mA h g^{-1} (half of theoretical capacity), corresponding to:

$$LiCo^{3+}O_2 \rightarrow Li_{0.5}Co^{3+}{}_{0.5}Co^{4+}{}_{0.5}O_2 + 0.5Li^+ + 0.5e^- .$$

Substitution of one or more transition metal ions in $LiCOO_2$ has been explored to improve the electrochemical performance.

The structure of LLOs is described as a solid solution or nano composite of Li_2MnO_3 (*C2/m*) and $LiMO_2$ (*R-3m*). The electrochemical deinsertion/insertion behaviour of LLOs is complex and also not yet understood completely.

All the previous investigations of cathode materials for LIBs were concentrated on 3d transition metals. Considering several accessible oxidation states and the versatile redox chemistry of ruthenium, a 4d metal, we proposed to investigate ruthenium substitution in the layered transition metal oxides, both $LiCoO_2$ type and LLOs.

The present thesis consists of four parts. After a brief introduction (Part 1), Part 2 is devoted to materials for Li-ion battery cathode, consisting of three Chapters 2.1, 2.2 and 2.3. In **Chapter 2.1**, we describe the synthesis, crystal structure, magnetic and electrochemical characterization of new $LiCoO_2$ type rock salt oxides of formula, $Li_3M_2RuO_6$ (M = Co, Ni). The M = Co oxide adopts the $LiCoO_2$ (*R-3m*) structure, whereas the M = Ni oxide also adopts a similar layered structure related to Li_2TiO_3. Magnetic susceptibility measurements reveal that in $Li_3Co_2RuO_6$, the oxidation states of transition metal ions are Co^{3+}, Co^{2+} and Ru^{4+}, whereas in $Li_3Ni_2RuO_6$, the oxidation states are Ni^{2+} and Ru^{5+}. $Li_3Co_2RuO_6$ orders antiferromagnetically at ~10K. On the other hand, $Li_3Ni_2RuO_6$ presents a ferrimagnetic behaviour with a Curie temperature of ~100K. Electrochemical Li-deinsertion/insertion studies show that high first charge capacities (between ca.160 and 180 mA h g^{-1}) corresponding to ca.2/3 of theoretical capacity are reached albeit, in both cases, capacity retention and cyclability are not satisfactory.

Chapter 2.2 presents a study of new ruthenium containing LLOs, Li_3MRuO_5 (M = Co and Ni). Both the oxides crystallize in the layered LLO type $LiCoO_2$ (α-$NaFeO_2$) structure consisting of $Li[Li_{0.2}M_{0.4}Ru_{0.4}]O_2$ layers. Magnetic susceptibility data suggest that the oxidation states of transition metals are $Li_3Co^{3+}Ru^{4+}O_5$ for the M = Co compound and $Li_3Ni^{2+}Ru^{5+}O_5$ for the M = Ni compound. Electrochemical investigations of lithium deintercalation–intercalation behaviour reveal that both Co and Ni phases exhibit attractive specific capacities of ca. 200 mA h g^{-1} at an average voltage of 4 V, that has been interpreted as due to the oxidation of Co^{3+} and Ru^{4+} in Li_3CoRuO_5 and Ni^{2+} to Ni^{4+} in the case of Li_3NiRuO_5. Thus, we find that

ruthenium plays a favourable role in LLOs than in non-LLOs in stabilizing higher reversible electrochemical capacities.

In **Chapter 2.3**, we describe the synthesis, crystal structure and lithium deinsertion–insertion electrochemistry of two new LLOs, Li_3MRuO_5 (M = Mn, Fe) which are analogs of the oxides described in Chapter 2.2. The Li_3MnRuO_5 oxide adopts a structure related to Li_2MnO_3 (*C2/m*), while the Li_3FeRuO_5 oxide adopts a near-perfect $LiCoO_2$ (*R-3m*) structure. Lithium electrochemistry shows typical behaviour of LLOs for both oxides, where participation of oxide ions in the electrochemical processes is observed. A long first charge process with capacities of 240 mA h g^{-1} (2.3 Li per f.u.) and 144 mA h g^{-1} (1.38 Li per f.u.) is observed for Li_3MnRuO_5 and Li_3FeRuO_5, respectively. Further discharge–charge cycling points to partial reversibility. X-ray photoelectron spectroscopy (XPS) characterisation of both pristine and electrochemically oxidized Li_3MRuO_5 reveals that in the Li_3MnRuO_5 oxide, Mn^{3+} and Ru^{4+} are partially oxidized to Mn^{4+} and Ru^{5+} in the sloping region at low voltage, while in the long plateau, O^{2-} is also oxidized. In the Li_3FeRuO_5 oxide, the oxidation process appears to affect only Ru (4+ to 5+ in the sloping region) and O^{2-} (plateau), while Fe seems to retain its 3+ state.

Another characteristic feature of TMs is formation of **several coloured solid materials** where *d–d transitions, band gap transitions* and *charge transfer transitions* are involved in the colouration mechanism. Coloured TM oxides absorbing visible light find important applications as visible light photocatalyst (for example, yellow $BiVO_4$ for solar water splitting and red $Sr_{1-x}NbO_3$ for oxidation of methylene blue) and inorganic pigments [for example, Egyptian blue ($CaCuSi_4O_{10}$), Malachite green ($Cu_2CO_3(OH)_2$), Ochre red (Fe_2O_3)]. Pigments are applied as colouring materials in inks, dyes, paints, plastics, ceramic glazers, enamels and textiles. In this thesis, we have focused on the coloured TM oxides for possible application as inorganic pigments.

Generally, colours arise from electronic transitions that absorb visible light. Colours of the inorganic pigments arise mainly from electronic

transitions involving TM ions in various ligand fields and charge transfer transitions governed by different selection rules. The ligand field *d–d transitions* are parity forbidden but are relaxed due to various reasons, such as distortion (absence of center of inversion) and vibronic coupling. The d-electrons can be excited by light absorption in the visible region of the spectrum imparting colour to the material. Charge transfer transitions in the visible region are not restricted by the parity selection rules and therefore give intense colours.

Here we have investigated the colours of manganese in unusual oxidation state (Mn^{5+}) as well as the colours of different 3d-TM ions in distorted octahedral and trigonal prismatic sites in appropriate colourless crystalline host oxides. These results are discussed in Part 3 of the thesis.

In **Chapter 3.1**, we describe a blue/green inorganic material, $Ba_3(P_{1-x}Mn_xO_4)_2$ (I) based on tetrahedral $Mn^{5+}O_4$:3d^2 chromophore. The solid solutions (I) which are sky-blue and turquoise-blue for $x \leq 0{\cdot}25$ and dark green for $x \geq 0{\cdot}50$, are readily synthesized in air from commonly available starting materials, stabilizing the $Mn^{5+}O_4$ chromophore in an isostructural phosphate host. We suggest that the covalency/ionicity of P–O/Mn–O bonds in the solid solutions tunes the crystal field strength around Mn(V) such that a blue colour results for materials with small values of *x*. The material could serve as a nontoxic blue/green inorganic pigment.

In **Chapter 3.2**, an experimental investigation of the stabilization of the turquoise-coloured $Mn^{5+}O_4$ chromophore in various oxide hosts, viz., $A_3(VO_4)_2$ (A = Ba, Sr, Ca), YVO_4, and Ba_2MO_4 (M = Ti, Si), has been carried out. The results reveal that substitution of $Mn^{5+}O_4$ occurs in $Ba_3(VO_4)_2$ forming the entire solid solution series $Ba_3(V_{1-x}Mn_xO_4)_2$ ($0 < x \leq 1.0$), while, with the corresponding strontium derivative, only up to about 10% of $Mn^{5+}O_4$ substitution is possible. $Ca_3(VO_4)_2$ and YVO_4 do not stabilize $Mn^{5+}O_4$ at all. With Ba_2MO_4 (M = Ti, Si), we could prepare only partially substituted materials, $Ba_2M_{1-x}Mn^{5+}{}_xO_{4+x/2}$ for x up to 0.15, that are turquoise-coloured. We rationalize the results that a large stabilization of the O 2p-valence band

states occurs in the presence of the electropositive barium that renders the Mn^{5+} oxidation state accessible in oxoanion compounds containing PO_4^{3-}, VO_4^{3-}, etc. By way of proof-of-concept, we synthesized new turquoise-coloured $Mn^{5+}O_4$ materials, $Ba_5(BO_3)(MnO_4)_2Cl$ and $Ba_5(BO_3)(PO_4)(MnO_4)Cl$, based on the apatite – $Ba_5(PO_4)_3Cl$ – structure.

Chapter 3.3 discusses crystal structures, and optical absorption spectra/colours of 3d-transition metal substituted lyonsite type oxides, $Li_3Al_{1-x}M^{III}_x(MoO_4)_3$ ($0< x \leq 1.0$) (M^{III} = Cr, Fe) and $Li_{3-x}Al_{1-x}M^{II}_{2x}(MoO_4)_3$ ($0< x \leq 1.0$) (M^{II} = Co, Ni, Cu). Crystal structures determined from Rietveld refinement of PXRD data reveal that in the smaller trivalent metal substituted lyonsite oxides, M^{III} ions occupy the octahedral (8d, 4c) sites and the lithium ions exclusively occur at the trigonal prismatic (4c) site in the orthorhombic (*Pnma*) structure; on the other hand, larger divalent cations (Co^{II}/Cu^{II}) substituted derivatives show occupancy of Co^{II}/Cu^{II} ions at both the octahedral and trigonal prismatic sites. We have investigated the colours and optical absorption spectra of $Li_3Al_{1-x}M^{III}_x(MoO_4)_3$ (M^{III} = Cr, Fe) and $Li_{3-x}Al_{1-x}M^{II}_{2x}(MoO_4)_3$ (M^{II} = Co, Ni, Cu) and interpreted the results in terms of average crystal field strengths experienced by M^{III}/M^{II} ions at multiple coordination geometries. We have also identified the role of metal-to-metal charge transfer (MMCT) from the partially filled transition metal 3d orbitals to the empty Mo – 4d orbitals in the resulting colours of these oxides.

The ABO_3 perovskite structure consists of a three dimensional framework of corner shared BO_6 octahedra in which large A cation occupies dodecahedral site, surrounded by twelve oxide ions. The ideal cubic structure occurs when the Goldschmidt's tolerance factor, $t = (r_A + r_O)/\{\sqrt{2}(r_B + r_O)\}$, adopts a value of unity and the A–O and B–O bond distances are perfectly matched. The BO_6 octahedra tilt and bend the B – O – B bridges co-operatively to adjust for the non-ideal size of A cations, resulting deviation from ideal cubic structure to lower symmetries. Ordering of cations at the A and B sites of perovskite structure is an important phenomenon. Ordering of

B site cations in double ($A_2BB'O_6$) and multiple ($A_3BB'_2O_9$) perovskites give rise to newer and interesting materials properties.

Depending upon the constituent transition metals and ordering, double perovskite oxides exhibit a variety of magnetic behaviour such as ferromagnetism, ferrimagnetism, antiferromagnetism, spin-glass magnetism and so on. We also have coupled magnetic properties such as magnetoresistance (Sr_2FeMoO_6), magnetodielectric (La_2NiMnO_6) and magnetooptic (Sr_2CrWO_6) behaviour. Here we have investigated new magnetically frustrated double perovskite oxides of the formula $Ln_3B_2RuO_9$ (B = Co, Ni and Ln = La, Nd).

The **Chapter 4.1** describes $Ln_3B_2RuO_9$ (B = Co, Ni and Ln = La, Nd) oxides (prepared by a solid state metathesis route) which adopt a monoclinic ($P2_1/n$) $A_2BB'O_6$ double perovskite structure, wherein the two independent octahedral 2c and 2d sites are occupied by B^{2+} and ($B^{2+}_{1/3}Ru^{5+}_{2/3}$) atoms, respectively. Temperature dependence of the molar magnetic susceptibility plots obtained under zero field cooled (ZFC) condition exhibit maxima in the temperature range 25–35K, suggesting an antiferromagnetic interaction in all these oxides. $Ln_3B_2RuO_9$ oxides show spin-glass behavior and no long-range magnetic order is found down to 2 K. The results reveal the importance of competing nearest neighbour (NN), next nearest neighbour (NNN) and third nearest neighbour (third NN) interactions between the magnetic Ni^{2+}/Co^{2+} and Ru^{5+} atoms in the partially ordered double perovskite structure that conspire to thwart the expected ferromagnetic order in these materials.